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## PATENT SPECIFICATION

(11)

1 444 204

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- (21) Application No. 4283/74 (22) Filed 30 Jan. 1974 (19)  
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(54) CLEAR PERFUMED POLYAMIDE RESIN AND METHOD OF  
 MAKING IT

- (71) We, POLAR'S FRUTAL WORKS, INC.,  
 a corporation of the State of New York,  
 United States of America, of the City of  
 Middletown, New York, New York 10904,  
 5 United States of America, do hereby declare  
 the invention, for which we pray that a  
 patent may be granted to us, and the method  
 by which it is to be performed, to be partic-  
 10 ularly described in and by the following  
 statement:—
- The present invention relates to materials  
 composed of clear substantially solvent-free  
 polyamide resins containing perfume oils and  
 to methods of making the same. By 'solvent-  
 15 free' we mean free from solvent other than  
 the resins and perfume oils themselves.
- Polyamide resins are known which vary  
 from clear to opaque and from smearable  
 semisolids to very hard bodies of high ten-  
 20 sile, compressive and impact strength.
- It has been proposed to make perfumed  
 objects of soft gels containing polyamide  
 resin, e.g., a clear lipstick that can be  
 25 smeared on the lips and a clear candle that  
 on burning volatilizes the perfume and adds  
 fragrance to the atmosphere around it. In  
 these products the polyamide is used in  
 30 relatively small proportions as a gelling  
 agent in a system which otherwise contains  
 a large proportion of solvent liquid, a dye  
 or pigment, and a relatively small amount of  
 fragrance. The gels are soft, spreadable and  
 35 deformable at room temperature.
- It has been discovered that a clear solid,  
 i.e., relatively rigid, polyamide resin material  
 containing perfume oil can be made without  
 substantial amounts of added solvent by  
 40 proper selection of the polyamide resin and  
 by following certain making procedures as  
 set forth hereinbelow.
- According to the present invention we pro-  
 vide a clear solid thermoplastic resin material  
 consisting substantially of a thermo-  
 plastic polyamide resin containing perfume  
 oil in an amount not exceeding 30 per cent  
 45
- by weight based on the resin plus the per-  
 fume oil, and being substantially free of  
 solvent, said thermoplastic polyamide resin  
 being a fatty polyamide which softens within  
 a range of 10 to 15°C on heating in the 50  
 range of 100—200°C., has a sharp decrease  
 in viscosity at temperatures above its softening  
 range and has a molecular weight within  
 the range 6000 to 9000.
- The resin used in the invention must be  
 55 optically clear at room temperature to yield  
 an optically clear body containing perfume  
 oil. In general the polyamide resins having  
 this desired clarity and suitable physical  
 properties are fatty polyamides which have  
 60 molecular weights within the range of 6,000  
 to 9,000 and are based on condensation of  
 polyamines, especially diamines and tri-  
 amines, with high molecular weight dicar-  
 boxylic acids, especially of the type which  
 65 result from dimerization of diunsaturated  
 carboxylic acids, e.g., condensation products  
 of dimerized linoleic acid and ethylene di-  
 amine. They are characterized by substan-  
 tial retention of their room temperature  
 70 hardness on heating until very near the  
 melting or softening temperature which is  
 relatively sharp, e.g., over a range of 10—  
 15°C. within the range of 100 to 200°C.,  
 depending on the molecular weight, and by  
 75 a sharp decrease in viscosity at tempera-  
 tures above the melting or softening point or  
 range. The optical clarity is believed to be  
 due to the solubility of all of the components  
 in the resin. Methods of making such resins  
 80 are disclosed in the expired U.S. Patent  
 2,379,413. In contrast, some well known  
 polyamide resins of the nylon type, e.g.,  
 nylon 6, which are not suitable for the pres-  
 ent invention have higher molecular weights  
 85 and are opaque, probably because the com-  
 ponents of the mixtures are not mutually  
 soluble.
- A clear resin suitable for use in the in-  
 vention is made by reacting dimerized linoleic 90

- acid with ethylene diamine to produce a product of the formula
- $$\text{HO}(-\text{OC}-\text{R}-\text{CONHR}'-\text{NH}_2)_n\text{H}$$
- in which R is a hydrocarbon group of an indeterminate configuration containing 34 carbon atoms and R' is  $-\text{CH}_2\text{CH}_2-$  and which has the following typical properties:
- |    |                                 |            |
|----|---------------------------------|------------|
| 5  | Softening point (Ball and Ring) | 110—115°C. |
| 10 | Viscosity (Brookfield)          |            |
| 15 | Poises at 150°C                 | 30—35      |
|    | Poises at 160°C                 | 21—27      |
| 20 | Tensile Strength (P.S.I.)       | 1500—2000  |
|    | Color (Gardner, 40% solution)   | 4—7        |
|    | Specific Gravity                | 0.97       |
- It is clear amber in color, non-tacky at room temperature, has a relatively sharp melting point and is thermoplastic with a narrow heat seal range. It exhibits good adhesion to a variety of substrates and can be applied to substrates from solution or from a melt. Thin films show good flexibility. The resin is conveniently prepared for commercial use in diced form for supplying either batch heating vessels or molding machines. Such a resin in diced form is available commercially from General Mills, Inc., under the name Versamid 930 ("Versamid" is a registered Trade Mark). Versamid 940 is similar thereto but has slightly lower viscosity, tensile strength and elongation. Versamid 1635 also is similar thereto but has a lighter color and lower inherent color. Resins having these properties are excellently suitable for the present invention. Further description of the suitable resins is unnecessary because they are well known to those skilled in the art and have been extensively described in literature published by General Mills on Versamid polyamide resins, in text books, encyclopedias, and other technical publications.
- The fragrances suitable for the present invention, sometimes called perfume oils, are complex mixtures of volatile compounds ing esters, ethers, aldehydes, alcohols, unsaturated hydrocarbons, e.g., terpenes, which are well known to persons skilled in the fragrance art and need not be further identified. Their use as to type and proportion in the present invention is limited only by solubility in the resin to produce a clear product.
- The process of making the clear perfumed resin materials of the invention comprises melting the resin by heating it until sufficiently molten to be stirrable and pourable. For a resin having the properties specified above this condition obtains when the temperature is within the range of 100—200°C.
- and preferably below about 160°C. The perfume oil is added to the liquid resin and blended therewith, e.g., by stirring or other mechanical agitation until a uniform mixture or blend is formed. No solvent for the resin and the perfume oil need be added at any time during the process. The mixture is cooled promptly after thorough mixing to solid condition, preferably rapidly as by quenching in cold water or by pouring onto or bringing into contact with a cold metal surface to which it is not adherent. The product obtained by this process is optically clear, has a high polished surface and a strong fragrance that faithfully represents the odor of the perfume oil, especially when the resin used has low inherent odor. These products have good optical stability and retain a substantial proportion of the fragrance for months.
- The perfumed materials of the present invention may be formed into a wide variety of useful objects such as jewellery, e.g., pendant earrings, pins or brooches; decorative castings such as birds, animals, or abstract objects; coatings on various substrates, e.g., on Christmas tree ornaments and electric light bulbs such as Christmas tree lights where the heat of the lighted filament increases the volatility and rate of transfer to the atmosphere of the perfume oil from the resin coating. Such coated Christmas tree ornaments and lights can be scented with pine oil, for example, to add an aspect of reality when used on artificial Christmas trees.
- The proportion of perfume oil to resin may vary from small but effective amounts of the order of a percent or so up to the maximum amount the resin can contain and still maintain optical clarity which is up to 30% by weight based on the resin plus the perfume oil. In general it is preferred to use about 12% which is an optimum value balancing the proportion of perfume oil recovered in the product against the length of time period over which the objects give off a fragrant odor.
- The following specific Example illustrates the method and product of the invention.
- EXAMPLE**
- In a vessel associated with a source of heat a quantity of diced Versamid 930 amounting to 88 parts by weight is heated to about 130°C. at which temperature the resin is a pourable and stirrable body of liquid. A quantity of a perfume oil having a floral bouquet with a woody background amounting to 12 parts by weight is stirred into the liquid resin until a uniform blend is achieved at which time the mixture is poured into standing cold water to facilitate rapid cooling and solidification to minimize loss of perfume oil. The product is clear amber solid having a highly polished surface

- with a pronounced odor faithfully reproducing the fragrance of the perfume oil used in making it. The product is in the form of a solid solution which lends itself to molding under heat and pressure into objects of jewellery such as pendant earrings, to casting in molds to form decorative art objects, and to spreading as a film on substrates such as Christmas tree ornament or glass light bulbs.
- Similar results are achieved using Versamid 1635 and other perfume oil fragrances.
- In general it is advantageous to carry out the mixing operation in a closed vessel, preferably a pressure vessel, in order to prevent substantial loss of perfume oil by vaporization. Where the final objects are made by molding, e.g., injection molding, the perfume oil is preferably introduced directly into the resin in the feed supply line, preferably after the resin is liquified, and uniformly blended into the resin therein.
- WHAT WE CLAIM IS:—
1. A clear solid thermoplastic resin material consisting substantially of a thermoplastic polyamide resin containing perfume oil in an amount not exceeding 30 per cent by weight based on the resin plus the perfume oil, and being substantially free of solvent, said thermoplastic polyamide resin being a fatty polyamide which softens within a range of 10 to 15°C on heating in the range of 100—200°C, has a sharp decrease in viscosity at temperatures above its softening range and has a molecular weight within the range 6000 to 9000.
2. A resin material as claimed in Claim 1, in which the perfume oil is in the resin as a solid solution.
3. A resin material as claimed in Claim 1 or 2, which is part of a piece of jewellery.
4. A resin material as claimed in Claim 1 or 2, which is in the form of a decorative casting.
5. A resin material as claimed in Claim 1 or 2, which is a coating on a substrate.
6. A resin material as claimed in Claim 5, in which the substrate is in the form of an ornament.
7. A resin material as claimed in Claim 5, in which the substrate is in the form of an electric light bulb.
8. A clear polyamide resin material according to Claim 1, substantially as described with reference to the foregoing Example.

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